Effects of Ti-based catalysts on hydrogen desorption kinetics of nanostructured magnesium hydride

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Abstract

In the present work, the synergetic effect of Ti-based catalysts (TiH\(_2\) and TiO\(_2\) particles) on hydrogen desorption kinetics of nanostructured magnesium hydride was investigated. Nanostructured 84 mol% MgH\(_2\)-16 mol% TiH\(_2\) nanoparticles were prepared by high-energy ball milling and subjected to thermal analyses. Evaluation of the absorption/desorption properties revealed that the addition of the Ti-based catalysts significantly improved the hydrogen storage performance of MgH\(_2\). A decrease in the decomposition temperature (as high as 100 °C) was attained after co-milling of MgH\(_2\) with the Ti-based catalysts. Meanwhile, solid-state chemical reactions between MgH\(_2\) and TiO\(_2\) nanoparticles during co-milling slightly decreased the maximum hydrogen capacity. It was also found that formation of micro-cracks at the particle surfaces during thermal cycling enhanced the H-kinetics. Isothermal and non-isothermal thermal analysis revealed that the addition of Ti-catalysts reduced the decomposition activation energy of MgH\(_2\) by 20–30 kJ/mol.

Graphical abstract

Effects of Ti-based catalysts on hydrogen desorption kinetics of nanostructured magnesium hydride

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ABSTRACT

In the present work, the synergetic effect of Ti-based catalysts (TiH₂ and TiO₂ particles) on hydrogen desorption kinetics of nanostructured magnesium hydride was investigated. Nanostructured 84 mol% MgH₂–10%mol TiH₂–6%mol TiO₂ nanocomposite powder was prepared by high-energy ball milling and subjected to thermal analyses. Evaluation of the absorption/desorption properties revealed that the addition of the Ti-based catalysts significantly improved the hydrogen storage performance of MgH₂. A decrease in the decomposition temperature (as high as 100 °C) was attained after co-milling of MgH₂ with the Ti-based catalysts. Meanwhile, solid-state chemical reactions between MgH₂ and TiO₂ nanoparticles during co-milling slightly decreased the maximum hydrogen capacity. It was also found that formation of micro-cracks at the particle surfaces during thermal cycling enhanced the H-kinetics. Isothermal and non-isothermal thermal analysis revealed that the addition of Ti-catalysts reduced the decomposition activation energy of MgH₂ by 20–30 kJ/mol.

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Introduction

There have been great concerns in recent years over the issue of pollution and global warming. Hydrogen is a sustainable and non-polluting source of energy that can be used for both stationary and mobile applications [1]. Besides its advantages as a zero-emission energy source, there are still substantial technological challenges for hydrogen usage, particularly in mobile applications [2]. Therefore, development of safe, inexpensive and light-weight storage facilities is indeed essential.

Due to high gravimetric and volumetric storage capacities and safe operating pressures, metal hydrides have attracted...
significant attention for hydrogen storage applications [3,4]. Magnesium and its alloys are potentially promising candidates for hydrogen storage application because of their lightweight, low cost, availability, and reversibility with a hydrogen capacity up to 7.6 wt% [1]. However, the high thermodynamic stability of MgH₂ at moderate temperatures (<300 °C [2]) hinders its application for hydrogen storage. To improve the slow H-kinetics of MgH₂ and to decrease its sorption/desorption temperature, several approaches have been examined [3,5–10]. Doping with transition metals (TM) [5], catalytic activation by metal oxides [9], nanostructuring through mechanical milling [3,6], and thin film technology [7,8,10] have been utilized. For instance, doping of MgH₂ with Ni through high-energy mechanical milling significantly enhances the H-kinetics through reducing of Mg–H bonding energy [11] and shortening of the diffusion pathway via nanometer-sized grains [3,12]. Catalytic mechanism of transition metal oxides is attributed to more defect sites and the interaction between the TM ions and hydrogen [9]. Synergistic effects of doping, nanostructuring and metal oxide catalytic effect have also been reported [13,14].

Recently, catalytic effects of titanium and its compounds on hydrogenation/dehydrogenation of MgH₂ have attracted interest. Results have shown a significant enhancement of the H-kinetics by Ti [5,12,15], TiH₂ [16–18], and TiO₂ [6,19,20]. Lu et al. [16] reported a reversible hydrogen storage with a cyclic capacity of 6 wt% in nanostructured MgH₂–0.3TiH₂ powder. The powder was prepared by high-energy high-pressure reactive milling and demonstrated high cycle stability with no loss of capacity over 80 cycles. Mahmoudi et al. [21,22] examined the effect of Ti-based alloys on desorption properties of MgH₂. The addition of Ti alloys was performed via both mechanical alloying and combined vacuum melting/mechanical alloying procedures. Although a loss in the hydrogen storage capacity was noticed, the improvement in H-kinetics was remarkable. Croston et al. [19] reported the catalytic effect of nanometric TiO₂ particles on desorption kinetics of MgH₂. The critical role of the particle size and specific surface area of the catalyst was shown. Anatase and rutile phases reduced desorption onset temperature at similar rates. Ninety percent hydrogen desorption at 300 °C and 0.1 bar hydrogen pressure was also demonstrated.

The aim of the present work is to study the synergetic effect of TiO₂ and TiH₂ addition on desorption behavior of MgH₂. The potential benefit of this catalytic combination could be enhanced H-kinetics due to simultaneous effects of increased defect sites and Ti/H interactions on the activation energy of decomposition. To the best knowledge of the authors, the combined effect of titanium oxide with titanium hydrides on the dehydrogenation kinetics of nanostructured MgH₂ has scarcely been studied. Nanostructured MgH₂ and 94 mol% MgH₂–10 mol% TiH₂–6 mol% TiO₂ nanocomposite powders were prepared by employing high-energy ball milling. The hydrogenation and dehydrogenation of the materials were examined through thermal analyses. It is shown that the Ti-based catalysts significantly reduce the activation energy of decomposition. The mechanisms of the improved dehydrogenation kinetics are discussed.

**Experimental procedure**

The starting materials were magnesium hydride (Alfa-Aesar, Germany), titanium hydride (Sigma–Aldrich, USA), and nanometric titanium dioxide particles (Ivonic Companies, USA). The characteristics of these materials are reported in Table 1. A mixture of MgH₂, TiH₂ and TiO₂ in molar ratio of 84 mol% MgH₂–10 mol% TiH₂–6 mol% TiO₂ was pre-mixed and mechanically milled by employing a Spex 8000 ball mill (SPEX, USA) under a high purity argon atmosphere. All the material handling was carried out in a glovebox under the argon atmosphere to prevent oxidation. A ball to powder weight ratio of 10:1 and a milling time of 4 h were utilized according to practices reported previously [13,14].

Scanning electron microscopy (SEM, Philips XL30, Netherlands) was employed to observe the morphological changes of the powders after mechanical milling. X-Ray diffraction (XRD) was carried out by using Cu–Kα radiation on a Philips PW1800 powder diffractometer (Philips Analytical, Netherlands) for phase characterization. Hydrogen absorption and desorption were examined by means of a volumetric Sievert apparatus. Isothermal analyses were performed on 500 mg powder in a temperature range of 300–425 °C as a function of time. Desorption curves were recorded under a hydrogen gas pressure of 0.2 and 1 atm. To evaluate dehydrogenation kinetics, the sample was first dehydrogenated at 400 ± 3 °C under vacuum (10⁻⁶ Torr) for 30 min to ensure complete desorption. Afterwards, absorption was performed under 20 bar hydrogen pressure at a desired temperature for various times. These cycles were repeated up to 3 times to study the effect of thermal cycling on hydrogen kinetics. Non-isothermal analyses were carried out on a Mettler-Toledo TGA/DSC Thermogravimetric Analyzer (Mettler-Toledo AG, Analytica, Switzerland) under a protective atmosphere at different heating rates of 2, 10 and 20 °C/min. A field-emission SEM (FESEM, Hitachi S4160, Japan) was utilized to observe changes in the powder particles after thermal cycling.

**Results and discussion**

**Dehydrogenation of MgH₂**

As a reference material, the desorption response of as-received MgH₂ powder was studied. Fig. 1a shows the dehydrogenation kinetics of magnesium hydride before

| Table 1 - Characteristics of raw materials used in this study. |
|-----------------------------------|--------|--------|-----------|--------|
| Material | Supplier | Purity (％) | Particle size | Comments |
| MgH₂ | Alfa Aesar | 98 | <105 μm | — |
| TiO₂ | Degussa | 99.5 | Average 21 nm | 80% Anatase/20% rutile |
| TiH₂ | Sigma–Aldrich | 98 | <44 μm | — |

mechanical milling at three different temperatures. No desorption at 375 ± 3 °C after 1500 s was obtained, revealing a relatively high stability of the metal hydride at the examined temperature. The decomposition enthalpy and entropy of MgH2 is in the range of 70–76.4 kJ/mol and 132–134.2 J/mol K [23]. Analysis of the decomposition temperature of MgH2 by HSC Chemistry software (Version 3.0, Outokumpu Research, Finland) shows that decomposition is thermodynamically feasible at around 300 °C (see Electronic Supplementary Document S1). Nevertheless, due to kinetic barriers, various experiments [1,14,18] have shown that the decomposition temperature could be as high as 350 °C and above. Our findings support previous observations and highlight the remarkable role of oxidation on desorption properties of magnesium hydride. It is known that very thin oxide layers covering the powder particles retard the nucleation of metallic magnesium on the surface of magnesium hydride particles [24]. Oxide layers with thickness of 3–4 nm could easily be formed during processing of magnesium powder under controlled inert gas atmospheres [24]. Experiments have also shown that complete dehydrogenation of MgH2 occurs at 400 ± 3 °C after 900 s (Fig. 1a). Although the decomposition temperature is high enough to overcome the kinetic barriers, a latent period of time is still required to begin desorption. Notably, desorption is happened quickly almost without a latent period of time at the higher temperature (425 ± 3 °C). Therefore, it seems that the oxide layers are still operative as nucleation barrier at moderate temperatures. To support this hypothesis, a thermal cycling was applied by affording dehydrogenation at 400 ± 3 °C for 30 min under high vacuum followed by hydrogenation under 20 atm hydrogen pressure at a desired temperature for various times (see Experimental procedure). Fig. 1b shows the results. Although the hydrogen storage capacity of MgH2 was reduced due to the formation of a surface shell [25] with much slower diffusion rate compared to Mg (500 times [26]), the latent period of time for desorption was almost diminished at 400 ± 3 °C. Fig. 2 shows FESEM images of the powder particles before and after thermal cycling. While initial particles had flake-like shape with rough surfaces, sponge-like particles containing several surface cracks were obtained after cycling. Intensive cracking of the particles during dehydrogenation is attributed to molar volume change of MgH2 to Mg that exerts compressive stresses. This phase transformation, which is accompanied with cracking of the particles, increases the specific surface area of the material, affecting the kinetics of dehydrogenation.

**Catalytic effects of Ti-based compounds**

To improve the H-kinetics of magnesium hydride, 84%mol MgH2−10%mol TiH2−6%mol TiO2 nanocomposite powder was prepared by mechanical alloying (MA). Since MA refines the grain structure of MgH2 and affects its H-Kinetics [3], MgH2 powder (without additives) was also milled under the same condition for comparison. Fig. 3 shows SEM micrographs of the powders. Continuous fracturing of the particles under the impact of moving balls refined the particles. The average size of particles for the nanocomposite (<1 μm) was notably smaller than that of the powder mixture (<100 μm). During MA, nanometer-sized inclusions can act as a milling agent as the hard particles accelerate fracturing of the base material [14]. The hard inclusions XRD pattern of MgH2 and MgH2−TiO2 powders after mechanical milling and annealing is shown in Fig. 4a. It is worthy to mention that a wide peak line broadening occurred upon high-energy mechanical milling; hence, the characteristic peaks of new possible phases could not be detected. To reveal possible interactions between MgH2 and TiO2 and formation of MgO, the powders were annealed at 350 °C for 100 min in a high pressure hydrogen atmosphere (10 atm) to prevent dehydrogenation. The pattern of the milled MgH2 powder did not exhibit any characteristic peaks that can be assigned to magnesium oxide. As reported elsewhere [1,13,27], high-pressure orthorhombic γ-MgH2 phase is commonly detectable in the milled MgH2 powder. Nevertheless, our results showed that in the annealed MgH2 powder, the γ-phase was not detected. On the other hand, high-energy mechanical milling of MgH2−TiO2 powder mixture promoted the formation of magnesium oxide (Fig. 4a). Therefore, these observations may suggest that the following reaction occurred upon MA:

\[3\text{MgH}_2 + 2\text{TiO}_2 = 3\text{MgO} + 2\text{TiH}_2 + \text{H}_2\text{O(g)}\]  

(1)

Thermodynamic analysis of this reaction at different temperatures using HSC software (Electronic Supplementary Document S2).

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Materials S2) showed that the oxidation of MgH2 was thermodynamically feasible. It is worthy to mention that due to high energy impeding of the balls during MA, temperature is locally raised and thus the oxidation of magnesium hydride becomes more likely. XRD pattern of 84%mol MgH2–10%mol TiH2–6%mol TiO2 powder before and after MA is shown in Fig. 4b. It seemed that no metastable ternary Mg–Ti–H phases were formed under the current experimental conditions, which influences the H-kinetics, as it will be explained later. Meanwhile, estimation of the average crystallite size of the MgH2 and nanocomposite powders by the peak broadening analysis (Williamson-Hall method) yielded values of 29 nm and 17 nm, respectively. The effect of hard inclusions on the grain refinement of MgH2 during MA was presented and discussed in details elsewhere [13].

Effects of mechanical alloying and addition of Ti catalysts on the dehydrogenation kinetics of MgH2 at $T = 300 \, ^\circ$C and $P_{H_2} = 0.2$ atm are shown in Fig. 5a. While the as-received MgH2 did not show desorption at the mentioned temperature, the milled MgH2 powder exhibited minor desorption (~0.3 wt%). On the other hand, catalytic activation by the Ti-base compounds led to significant enhancement of the H-kinetics. Here, the dehydrogenation temperature was depressed from 400 $^\circ$C to 300 $^\circ$C. The complete dehydrogenation also occurred in a shorter time, revealing a higher release rate. However, the hydrogen storage capacity per mass reduced to about 5 wt%, which is in good agreement with the estimated storage capacity of the composite powder based on its constituents (MgH2, TiH2, MgO, and TiO2). The improved H-kinetics of the investigated nanocomposite powder compared to the pristine...
before the conversion of MgH₂ to Mg is promoted improving the defects and disorders are preferred sites for diffusion. Thereby, the decomposition reaction is thermodynamically more favorable. Theoretical predications of the reaction enthalpy by Song et al. [29] also supported a change in the reaction thermodynamics of MgH₂–Ti system by weakening the Mg–H bond. On the other hand, at the expense of hydrogen content, Khrussanova et al. [30] have reported that Ti ‘pumps’ hydrogen to the magnesium surface, catalyzing the dehydrogenation process.

The hydrogenation of MgH₂ and the milled powders at T = 300 °C and P = 20 atm is shown in Fig. 5b. The as-received powder absorbed less than 1.5 wt% hydrogen after 60 s while hydrogen absorption for the nanostructured MgH₂ was ~4.5 wt%. It appears that nanostructuring and refinement of the particles significantly improve the hydrogenation process. High surface area enhances the chemisorption of H-atoms while nanometric grains promote diffusion rate. The addition of Ti-based compounds further improved the absorption kinetics at short times, i.e. ~4.5 wt% hydrogen uptake after 60 s. Similarly, finer particles and grain structure of the particles together with the ability of Ti to pump H to Mg surface and/or weakening of the Mg–H bond are operative. The short-cyclic absorption/desorption behavior of the composite powder was also examined (Fig. 6). No remarkable drop in the absorption capacity was noticed after 2 cycles (Fig. 6a). The cycling kinetics was also improved due to the formation of micro-cracks (Fig. 6b).

Kinetic study of the dehydrogenation process

In order to estimate the activation energy of decomposition of MgH₂ and the MgH₂–TiH₂–TiO₂ nanocomposite powders and to explore the synergetic effect of Ti-based catalyst, isothermal and non-isothermal analyses were performed. For the non-isothermal analysis, differential scanning calorimetric (DSC) at three heating rates (β) of 2, 10 and 20 °C/min were performed. Fig. 7a and b show the DSC curves of the examined materials. To important observations can be made. First, increasing the heating rate shifts the dehydrogenation peak to higher temperatures. Since the dehydrogenation is a kinetic event, both time and temperature are important. At faster heating rates, shorter transition times are observed at all temperatures; thereby, a shift in the transition temperature is seen. Second, the dehydrogenation temperatures at different heating rates are lower for the nanocomposite powder compared to the pristine MgH₂. This is attributed to the effect of Ti-based catalysts on the transition kinetics as explained above. In order to show this effect, the activation energy values were determined by Kissinger model [31]:

\[
\ln \left( \frac{\beta}{P^2_m} \right) = \ln \left( \frac{A_R}{E} J (\alpha_m) \right) - \frac{E}{RT_m},
\]

where T is the peak temperature, R gas constant, and A reaction constant. J(α_m) is the reaction model [32]. From the slope

MgH₂ powder can be attributed to the effect of Ti-based catalysts on the particle size, grain structure, and the strength of Mg–H bond in the presence of titanium. The Ti-based catalysts accelerated the size reduction of MgH₂ during MA (from around 29 to 17 nm). Since the H kinetics of MgH₂ should also be considered. Titanium hydride with an enthalpy formation of ~142.4 kJ/mol [28] is more stable than magnesium hydride (ΔH = ~75 kJ/mol [23]) while dehydrogenation occurs in a two-step process with high decomposition activation energies [22]. Lue et al. [16] has suggested that the Mg–H bond is weaker in Mg–Ti–H system; thereby, the decomposition reaction is thermodynamically more favorable. Theoretical predications of the reaction enthalpy by Song et al. [29] also supported a change in the reaction thermodynamics of MgH₂–Ti system by weakening the Mg–H bond. On the other hand, at the expense of hydrogen content, Khrussanova et al. [30] have reported that Ti ‘pumps’ hydrogen to the magnesium surface, catalyzing the dehydrogenation process.

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\ln \left( \frac{\beta}{P^2_m} \right) = \ln \left( \frac{A_R}{E} J (\alpha_m) \right) - \frac{E}{RT_m},
\]

where T is the peak temperature, R gas constant, and A reaction constant. J(α_m) is the reaction model [32]. From the slope
of \(1/T_{m1} - \ln[p/T_{m1}^2]\) plots (Fig. 7c), the activation energy of the MgH\(_2\) and MgH\(_2\)-TiH\(_2\)-TiO\(_2\) nanocomposite powders was determined. It was found that the Ti-catalysts reduced the activation energy of nanostructured MgH\(_2\) from 148 kJ/mol to 118 kJ/mol. For the isothermal analysis, Avrami-Erofeev [33] and shrinking-core [34] models were utilized for the nanostructured MgH\(_2\) and its nanocomposite, respectively. It is pertinent to point out that the appropriate kinetics models for the examined materials were determined by model fitting approach [35] (not explained here). The value of activation energy for the MgH\(_2\) powder was obtained \(\sim 129\) kJ/mol. The difference in activation energy values obtained by different models (129 and 118 kJ/mol; \(-8\)%) is originated from assumptions inherent in these models as well as different adopted experimental approaches (isothermal versus non-isothermal) and possibly experimental errors. Anyway, the analyses by different approaches indicate that the activation energy of MgH\(_2\) is decreased by about 20% when the Ti-based catalysts are introduced.

**Fig. 5** – Effects of Ti-based catalysts on the (a) desorption and (b) absorption of MgH\(_2\) at 300 °C. The hydrogen pressure for absorption and desorption was 20 and 0.2 atm, respectively.

**Fig. 6** – Thermal analysis of MgH\(_2\)-TiH\(_2\)-TiO\(_2\) composite powder showing the effect of short-cycling on (a) absorption and (b) desorption at 300 °C. The hydrogen pressure was 20 and 1 atm for (a) and (b), respectively.

**Conclusions**

In the present work, effects of Ti-based catalysts on the hydrogenation/dehydrogenation of nanostructured MgH\(_2\) powder were studied. MgH\(_2\) powder was co-milled with TiH\(_2\) and TiO\(_2\) particles and the H-kinetics of the prepared nanocomposite powder was investigated by thermal analysis. It was shown that co-milling of the Ti-based compounds with MgH\(_2\) powder decreased the decomposition temperature as high as 100 °C, as an indicator of the improvement in the kinetics of dehydrogenation process. Solid-state chemical re-actions between nano-metric TiO\(_2\) particles and MgH\(_2\) during co-milling were also noticed. Based on experimental observations, it was suggested that the addition of Ti-based catalysts to MgH\(_2\) increased the H-kinetics through multiple paths including: I) refinement of the grain structure (higher grain boundaries are available for the hydrogen diffusion); II) higher specific surface area of the particles (finer MgH\(_2\) particles are attained due to the presence of hard inclusions during MA); III) weakening of the Mg–H bond in the presence of Ti; IV) the role
of Ti on hydrogen diffusion to the particle surfaces. It was also shown that cyclic dehydrogenation of MgH2 enhanced its H-kinetics due to the formation of micro-cracks at the particle surfaces. Meanwhile, the nanocomposite powder exhibited short cyclic stability during dehydrogenation process. Model analysis of the dehydrogenation process determined decomposition apparent activation energy. Values of 148 and 118 kJ/mol were obtained for the MgH2 and nanostructured MgH2–10%mol TiH2–6%mol TiO2 nanocomposite, respectively.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.ijhydene.2014.10.078.

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